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# Engineering VO<sub>x</sub> structure by integrating oxygen vacancies for improved zinc-ion storage based on cation-doping regulation with electric density†

Juan Xu, \* Nengneng Han, Sihao Chen, Yahui Zhang, Yuezhou Jing, Pibin Bing and Zhongyang Li\*

Aqueous zinc-ion batteries (ZIBs) have attracted enormous attention for future energy-storage devices owing to their high theoretical capacity and environmental friendliness. However, obtaining cathodes with a high specific capacity and fast reaction kinetics remains a huge challenge. Herein, Cu-VO<sub>x</sub> material with a thin sheet microsphere structure composed of nanoparticles was prepared by a simple hydrothermal reaction, which improved reaction kinetics and specific capacity. Pre-embedding Cu<sup>2+</sup> into V<sub>2</sub>O<sub>5</sub> to introduce abundant oxygen vacancies extended the interlayer distance to 1.16 nm, weakened the effect of the V–O bonds, and improved the electrical conductivity and structural stability. At the same time, the influence of different valence metal ions (M = K<sup>+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Sn<sup>4+</sup>, Nb<sup>5+</sup>, and W<sup>6+</sup>) pre-embedded in V<sub>2</sub>O<sub>5</sub> was studied. Benefiting from a large interlayer spacing, high electrical conductivity, and excellent structural stability, the Cu-VO<sub>x</sub> electrode demonstrated a high specific capacity of 455.9 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup>. Importantly, when the current density was increased to 6 A g<sup>-1</sup>, the Cu-VO<sub>x</sub> electrode still achieved a high specific capacity of 178.8 mA h g<sup>-1</sup> and maintained a high capacity retention of 76.5% over 2000 cycles.

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## 1. Introduction

With the rapid development of the economy, the use of non-renewable energy (including natural gas, crude oil, and carbon) has also increased significantly, making the development of renewable energy imminent. In recent years, lithium-ion batteries have been widely used in the field of electric vehicles due to their high energy density.<sup>1–4</sup> However, the organic electrolyte in commercial lithium-ion batteries is flammable, which has resulted in several fire accidents in electric vehicles and limited the future use of lithium-ion batteries for energy storage.<sup>5–7</sup> Whereas, aqueous zinc-ion batteries, with a suitable redox potential of –0.76 V vs. hydrogen electrode and high theoretical specific capacity up to 820 mA h g<sup>-1</sup> (5854 mA h cm<sup>-3</sup>), are a safer and more stable alternative to lithium-ion batteries, making them the most promising energy-storage devices.<sup>8–11</sup>

Similar to lithium-ion batteries, the cathode material is critical to determine the performance of aqueous zinc-ion batteries. Vanadium-based oxides, manganese-based oxides, and Prussian blue analogs are the most commonly utilized cathode

materials for zinc-ion batteries.<sup>12–16</sup> Vanadium-based materials, such as vanadium pentoxide, have attracted considerable attention for their use in aqueous zinc-ion batteries owing to the merits of a layered structure and high specific capacity.<sup>17–19</sup> However, limitations, such as a lower average voltage and a structure that is prone to collapse during the charging/discharging cycling process, have hindered the development of vanadium-based materials.<sup>14,20</sup> In order to address the previous difficulties, researchers have implemented an ion pre-embedding technique to resolve the poor rate performance and sluggish reaction kinetics caused by the irreversible phase changes in their crystal structure. Pre-embedding metal ions not only increases the layer spacing of vanadium-based materials and promotes fast ion diffusion but also works as a “pillar” to improve the overall stability of the materials.<sup>21–23</sup> For example, Tong *et al.* employed a pre-intercalation technique involving iron and alkylammonium ions to create FeVO-12 composites effectively. The FeVO-12 compounds exhibited exceptional surface hydrophobicity and structural stability due to the combined influence of the two ions. The FeVO-12 electrode displayed a reversible specific capacity of 408 mA h g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup>. In addition, even after undergoing 1000 cycles at a high current density of 10 A g<sup>-1</sup>, the electrode maintained a high capacity retention rate of 90%.<sup>24</sup> Pang *et al.* successfully synthesized the new cathode material Mn<sub>0.2</sub>V<sub>8</sub>O<sub>20</sub>·1.12H<sub>2</sub>O (MnVO) using a hydrothermal reaction. The inclusion of water molecules and Mn<sup>2+</sup>

School of Electrical College, North China University of Water Resources and Electric Power, Zhengzhou 450045, P. R. China. E-mail: xujuan@ncwu.edu.cn, thzwave@163.com

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in the interlayer effectively helped avoid collapse of the cathode structure. The MnVO cathode exhibited a high specific capacity of 306.4 mA h g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup>. It also demonstrated a capacity retention of 86.4% after 1000 charging/discharging cycles at a current density of 2.0 A g<sup>-1</sup>, demonstrating its excellent cycling stability.<sup>25</sup> Qi's group investigated a cesium ion-inserted vanadium oxide nanorod (CsVO) as the cathode for zinc-ion batteries, which exhibited excellent electrochemical properties. The embedded cesium ions formed strong Cs–O bonds with oxygen atoms, while Cs doping made the interlayer interaction stronger. As a result, the Cs<sup>+</sup>-intercalated material demonstrated excellent multiplicity performances and an ultra-long cycling lifespan. The CsVO electrode showed a high specific capacity of 189.9 mA h g<sup>-1</sup> at 20 A g<sup>-1</sup>. Also, it exhibited outstanding cycling stability with 89% capacity retention over more than 10 000 cycles at a high current density of 20 A g<sup>-1</sup>.<sup>26</sup> Metal ions pre-embedded in vanadium oxides improve the electrical conductivity and structural stability, which is further strengthened by the strong coordination bonds established between the metal ions and oxygen atoms. Although the strategy of improving the electrochemical properties of vanadium oxides by pre-embedding various metal ions (Mg<sup>2+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup>)<sup>27–32</sup> has been extensively reported, the effect of ionic bonds formed between metal cations with different valence states and the host structure on the electrochemical properties of vanadium oxides remains unknown.

Based on the above considerations, we designed and prepared M-doped V<sub>2</sub>O<sub>5</sub> (M-VO<sub>x</sub>) with metal ions in different valence states. The doping of metal ions into V<sub>2</sub>O<sub>5</sub> enlarged the interlayer spacing to shorten the diffusion distance for Zn<sup>2+</sup>. Importantly, Cu-VO<sub>x</sub> materials with a thin sheet microsphere structure composed of nanoparticles were successfully prepared, with the largest interlayer distance of 1.16 nm. In addition, pre-embedding Cu<sup>2+</sup> into V<sub>2</sub>O<sub>5</sub> could introduce abundant oxygen vacancies to improve the electrical conductivity, weaken the effect of V–O bonds, and enhance the structural stability. As expected, the Cu-VO<sub>x</sub> electrode achieved a high specific capacity of 455.9 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup>, a favorable rate capacity of 178.8 mA h g<sup>-1</sup> at a high current density of 6 A g<sup>-1</sup>, and a high capacity retention of 76.5% after 2000 charging/discharging cycles, which demonstrated its promising cycling stability. Hence, the strategy of doping metal ions with the optimal electrical density can effectively improve the electrochemical performance of metal compounds through a synergistic effect, providing a new route for constructing aqueous zinc-ion batteries with high energy density.

## 2. Experimental section

### 2.1 Materials

Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>), potassium chloride (KCl), copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O), ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), tin chloride pentahydrate (SnCl<sub>4</sub>·5H<sub>2</sub>O), niobium chloride (NbCl<sub>5</sub>), tungsten chloride (WCl<sub>6</sub>), hydrogen

peroxide (H<sub>2</sub>O<sub>2</sub>), zinc foil, and zinc trifluoromethyl sulfonate (Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>) were purchased from Sinopharm Co. LTD. The deionized water (DI) used in the experiment was ultrapure water. All the raw materials were of analytical grade and used without further purification.

### 2.2 Materials synthesis

Various metal-ion-doped M-VO<sub>x</sub> materials were prepared by a green and pollution-free one-step hydrothermal method. Taking the preparation procedure for Cu-VO<sub>x</sub> materials as an example. Initially, the precursor solution was prepared by dissolving 2 mol V<sub>2</sub>O<sub>5</sub> into 50 ml deionized water. Subsequently, 2 mol CuCl<sub>2</sub>·2H<sub>2</sub>O was added to the solution and the solution was agitated constantly until it was fully dissolved. Subsequently, 2 ml hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was incrementally introduced into the solution dropwise while stirring for 30 min. Subsequently, the solution was put into a high-pressure reactor with a volume of 100 ml. The reaction was then conducted at 200 °C for 48 h. After cooling to room temperature, the obtained products were cleaned with deionized water and ethanol three times, respectively, and then dried at 80 °C. Also, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> materials were prepared using the same method as described above, with the only difference being the substitution of CuCl<sub>2</sub>·2H<sub>2</sub>O with KCl, FeCl<sub>3</sub>·6H<sub>2</sub>O, SnCl<sub>4</sub>·5H<sub>2</sub>O, NbCl<sub>5</sub>, or WCl<sub>6</sub> powder, respectively.

### 2.3 Characterization

The samples' surface morphology was characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM, Tecnai G20). Their chemical structures were analyzed by powder X-ray diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda = 1.54118 \text{ \AA}$ ) and X-ray photoelectron spectroscopy (XPS). A specific surface area analyzer (BET) (JWBK100) was used to characterize the specific surface area and pore-size distribution of the materials.

### 2.4 Electrochemical measurements

CR2025 coin cells were used to characterize the electrochemical properties of the materials. Here, the active material, conductive carbon black (Super-P), and polyvinyl tetrafluoroethylene (PVDF) were dissolved in a certain amount of *N*-methyl-2-pyrrolidone (NMP) solvent in a mass ratio of 7:2:1 and the solution was stirred at room temperature to obtain a homogeneous slurry. Then, the prepared slurry was scatter-coated on the carbon paper collector and after vacuum-dried at 80 °C overnight to prepare the working electrode. The prepared working electrode was used as the cathode, pretreated zinc foil was used as the anode, the Whatman membrane was used as the separator, and 3 M Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> solution was used as the electrolyte to assemble button-type aqueous zinc-ion batteries in the air. Among these, the active material loading of the working electrode was 1–2 mg. We tested the zinc-ion batteries using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (CHI

660E, Shanghai, China) and battery test system (LAND, CT2001, Shanghai, China).

### 3. Results and discussion

Cu-VO<sub>x</sub> compounds were prepared as shown schematically in Fig. 1 by a one-step hydrothermal method (see the Experimental section for details).

The morphologies of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> compounds were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a shows that the Cu-VO<sub>x</sub> material had a relatively dense microsphere structure due to the polymerization of several nanosheets with a diameter of about 4 μm. Further characterization revealed that the nanosheets were

composed of many uniform nanoparticles with a diameter of about 2–5 nm (Fig. 2b). This ultra-small nanoparticles structure is conducive to electrolyte penetration into the electrode material, shortening the ion-diffusion distance and enhancing the structural stability.<sup>33–35</sup> The TEM images in Fig. 2c also confirmed the thin sheet morphology of the surface of the Cu-VO<sub>x</sub> microspheres. In addition, Fig. S1† shows the morphology of the contrast samples. Among these, the K-VO<sub>x</sub> materials were composed of nanorods with a length of about 1 μm, and some nanorods showed a curved morphology. These relatively thick and stacked nanorods make it difficult to maintain structural stability during electrochemical reactions. The Sn-VO<sub>x</sub> materials also showed a nanorod structure, with a length of about 2 μm and a partial sheet form, which was formed by stacking nanorods. The Nb-VO<sub>x</sub> materials had a thick nanosheets structure, which randomly stacked

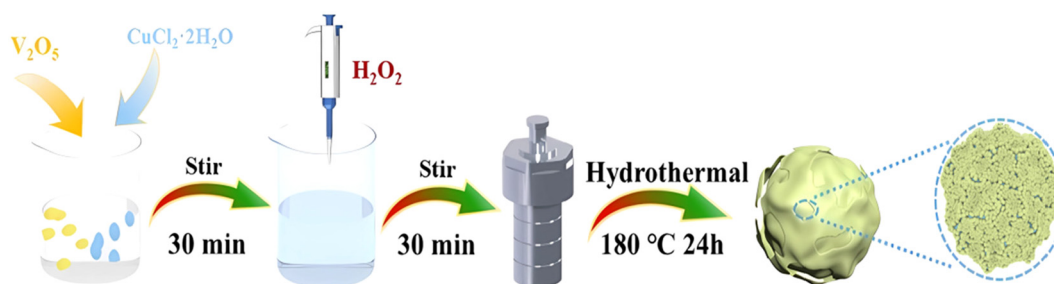


Fig. 1 Schematic diagram for the preparation of the Cu-VO<sub>x</sub> compounds.

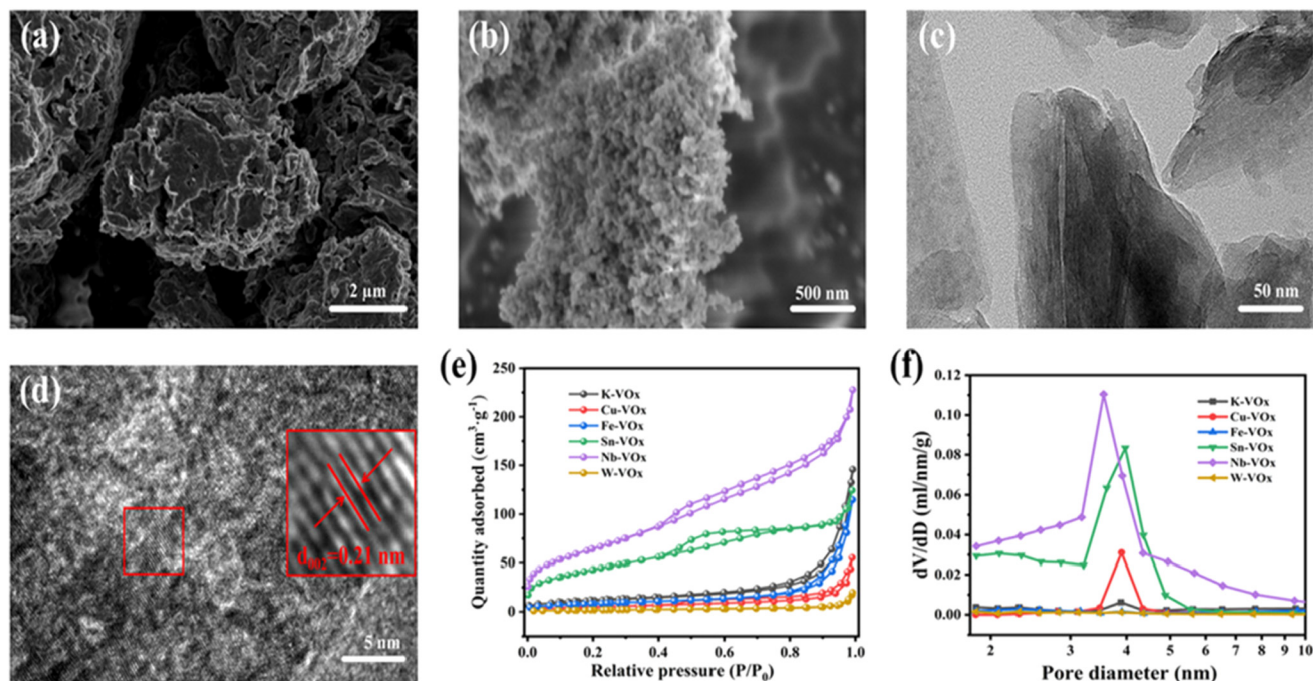
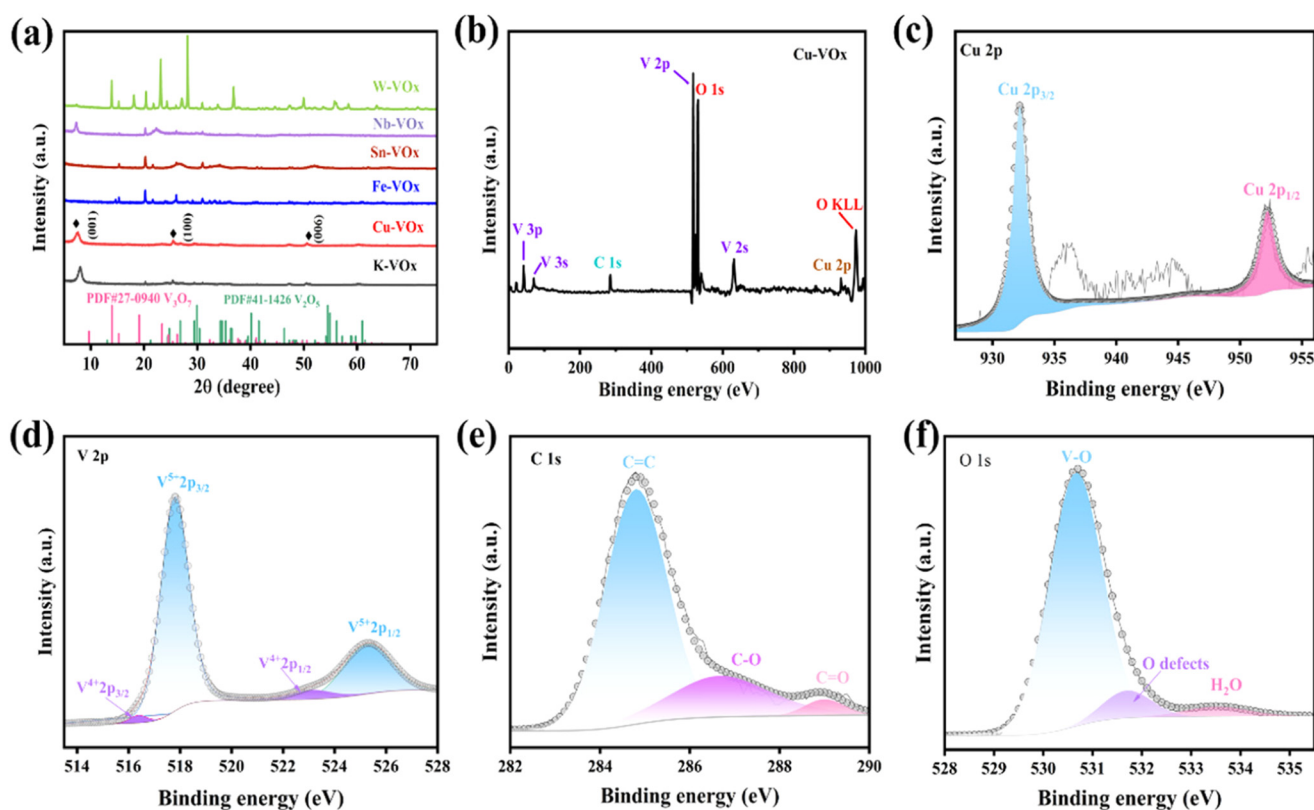


Fig. 2 (a and b) SEM images of the Cu-VO<sub>x</sub> compounds at different magnifications; (c) TEM and (d) HRTEM images of the Cu-VO<sub>x</sub> compounds; (e and f) N<sub>2</sub> adsorption–desorption curves and pore-size distribution curves of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> materials, respectively.

together, which was not conducive to the rapid transport of ions. The Fe-VO<sub>x</sub> materials displayed a nanoblock structure with multiple layers of nanosheets stacked on each other, which could easily collapse during the process of embedding Zn<sup>2+</sup>. The W-VO<sub>x</sub> materials also had a nanoblock structure stacked with multiple nanosheets, and the nanoblocks were larger, making it more difficult to maintain structural stability during zinc-ion transport.<sup>36</sup> Obviously, the thin sheet microsphere structure presented by Cu-VO<sub>x</sub> materials composed of nanoparticles could shorten the transport path of zinc ions, maintain the structural stability, and support excellent electrochemical performances, which was also consistent with the analysis of the electrochemical performance. Fig. 2d shows a HRTEM image of Cu-VO<sub>x</sub> with a lattice spacing of 0.21 nm, corresponding to the (002) crystal faces of VO<sub>x</sub> (JCPDS 41-1426). Fig. 2e and f show the BET adsorption-desorption curves and pore-size distribution curves of Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, Fe-VO<sub>x</sub>, and W-VO<sub>x</sub>, respectively. Their specific surface areas were 18.48, 41.73, 30.24, 157.42, 236.63, and 7.16 m<sup>2</sup> g<sup>-1</sup>, respectively, and their pore sizes were distributed at about 3–4 nm. The results showed that the embedding of different valence metal ions had little effect on the pore-size distribution of VO<sub>x</sub> materials but had a greater effect on the specific surface area. The large specific surface area of Cu-VO<sub>x</sub> materials increased the contact area of the electrolyte and the electrode surface, and

improved zinc-ion transport, which were conducive to the improvement of the electrochemical performances.<sup>37,38</sup>

XRD measurements were used to characterize the effects of different valence ions on the crystal structure of the VO<sub>x</sub> materials (Fig. 3a). Among these, the K-VO<sub>x</sub>, Cu-VO<sub>x</sub>, and Nb-VO<sub>x</sub> samples showed strong diffraction peaks for the (001) crystal plane at  $2\theta = 7.29^\circ$ , indicating that K<sup>+</sup>, Cu<sup>2+</sup>, and Nb<sup>5+</sup> had been successfully embedded in the interlayer of the VO<sub>x</sub> material. Using Bragg's formula, it was calculated that the crystal plane spacing of Cu-VO<sub>x</sub> increased from 0.44 nm to 1.16 nm, and the ion embedding not only increased the layer spacing but also improved the structural stability of the material.<sup>39</sup> However, no discernible diffraction peaks were seen at  $2\theta = 7.29^\circ$  in the XRD patterns of the Sn-VO<sub>x</sub>, Fe-VO<sub>x</sub>, and W-VO<sub>x</sub> materials. This perhaps could be attributed to the inability of Sn<sup>4+</sup>, Fe<sup>3+</sup>, and W<sup>5+</sup> to considerably enhance the interlayer spacing of the materials when integrated into the VO<sub>x</sub> materials. Furthermore, the XRD patterns of the materials did not exhibit any new phases upon embedding the ions with varying valence states in the VO<sub>x</sub> materials. Next, X-ray photoelectron spectroscopy (XPS) analysis of the VO<sub>x</sub> materials was performed and confirmed that Cu<sup>2+</sup> was indeed embedded in the VO<sub>x</sub> material (Fig. 3b); whereby the strong peaks that arose at binding energies of 932.3 and 952.3 eV in the Cu 2p XPS spectrum in Fig. 3c corresponded to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively. This suggested that the majority of the ions



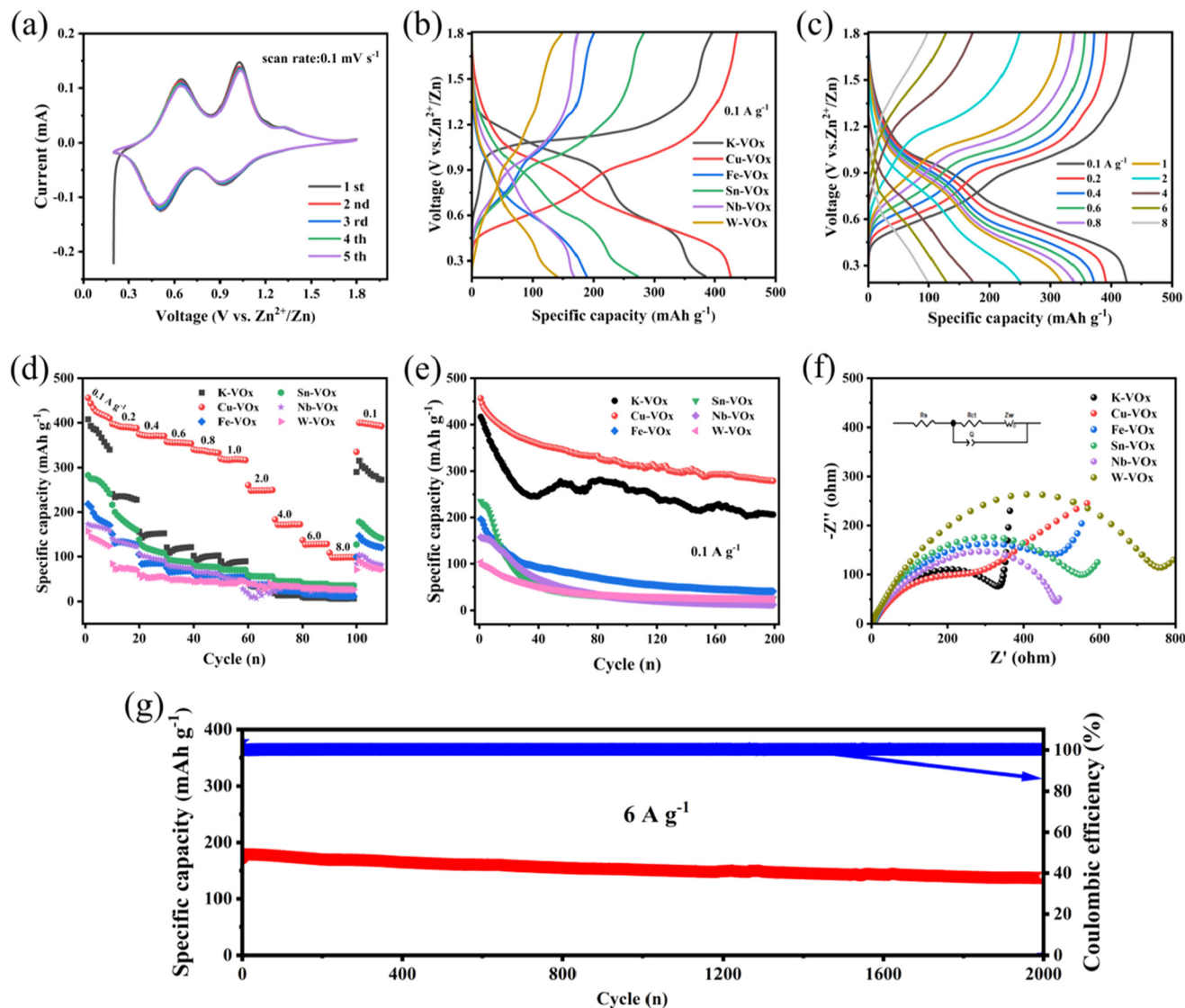
**Fig. 3** (a) XRD spectra of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> materials, respectively. (b, c, d, e and f) Full XPS spectrum, and Cu 2p, V 2p, C 1s, and O 1s spectra of the Cu-VO<sub>x</sub> materials, respectively.



buried in Cu-VO<sub>x</sub> were Cu<sup>2+</sup>. The V 2p XPS spectrum of the Cu-VO<sub>x</sub> material is displayed in Fig. 3d. The V(5+)–O stretching-related diffraction peaks with binding energies of 517.8 and 525.2 eV corresponded to V<sup>5+</sup> 2p<sub>3/2</sub> and V<sup>5+</sup> 2p<sub>1/2</sub>, respectively.<sup>40</sup> Furthermore, there were peaks at binding energies of 516.4 and 523.1 eV, which subsequently corresponded to V<sup>4+</sup> 2p<sub>3/2</sub> and V<sup>4+</sup> 2p<sub>1/2</sub>, respectively. The analysis mentioned above demonstrated that the Cu-VO<sub>x</sub> material had a low valence state of V<sup>4+</sup> and considerable V<sup>5+</sup>. According to the charge-conservation principle, oxygen vacancies must be created in the V<sub>2</sub>O<sub>5</sub> lattice to make up for the charge neutralization.<sup>41,42</sup> The XPS spectrum of C 1s is shown in Fig. 3e, displaying pronounced peaks at 284.8, 286.7, and 289 eV, corresponding to C=C, C–O and C=O bonds, respectively.<sup>43</sup> In the O 1s XPS spectrum in Fig. 2f, three obvious diffraction peaks at binding energies of 530.7, 531.7, and 533.5 eV could be seen, corresponding to lattice oxygen, oxygen vacancies, and adsorbed oxygen, respectively, further confirming the existence of oxygen vacancies, in which the proportion of oxygen vacancies was about 14.19%.<sup>26</sup> Incorporating Cu<sup>2+</sup> into VO<sub>x</sub> could increase the lattice spacing and introduce abundant oxygen vacancies. Benefiting from the synergistic effect, the Cu-VO<sub>x</sub> materials exhibited enhanced structural stability, high electrical conductivity, and excellent electrochemical performances.

The electrochemical performances of the Cu-VO<sub>x</sub> electrode and the contrast electrodes were studied with coin cells, in which the working electrodes, zinc foil, 3 M Zn (CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> electrolyte, and Whatman membrane served as the cathode, anode, electrolyte, and separator, respectively. Fig. 4a displays the cyclic voltammetry (CV) curves of the Cu-VO<sub>x</sub> electrode at a scan rate of 0.1 mV s<sup>-1</sup> during the initial five cycles. The CV curves for the initial five cycles showed similar patterns, suggesting the significant electrochemical reversibility of the Cu-VO<sub>x</sub> electrode. Furthermore, the CV curves of Cu-VO<sub>x</sub> exhibited two pair of redox peaks at 0.63/1.02 and 0.51/0.91 V. These peaks corresponded to the oxidation–reduction reactions of V<sup>5+</sup>/V<sup>4+</sup> and V<sup>4+</sup>/V<sup>3+</sup>, respectively.<sup>44,45</sup> For contrast, Fig. S2† shows the CV curves of the K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes. Among these, the CV curves of the Cu-VO<sub>x</sub> electrode had the largest area, indicating that the Cu-VO<sub>x</sub> electrode exhibited the relatively largest specific capacity. In the CV curves of the contrast electrodes, two pairs of obvious redox peaks were observed in all, and the corresponding voltage positions were basically the same. This indicated that the metal ions embedded in VO<sub>x</sub> increased the interlayer distance and electrical conductivity of the materials, but the contribution to the increase in the redox active sites was relatively weak, which was consistent with the analysis showing that the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, and Nb-VO<sub>x</sub> electrodes had relatively high specific capacities. Fig. 4b displays the galvanostatic charge–discharge (GCD) curves for the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, Fe-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes at a current density of 0.1 A g<sup>-1</sup>, with all showing a pronounced redox plateau. Also, the results were also consistent with the analyses of the CV curves in Fig. 4a and Fig. S2.† It is obvious that the Cu-VO<sub>x</sub> electrode had a higher specific capacity. The GCD curves of the Cu-VO<sub>x</sub> electrode at different current densities

are shown in Fig. 4c. The Cu-VO<sub>x</sub> electrodes achieved specific capacities of 455.9, 395.8, 373.2, 356.7, 339.2, 319.8, 248.1, 171.7, 126.7, and 97.9 mA h g<sup>-1</sup> at varied current densities of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, and 8.0 A g<sup>-1</sup>, respectively, demonstrating the electrodes outstanding rate properties. When the current density was recovered to 0.1 A g<sup>-1</sup>, the Cu-VO<sub>x</sub> electrode could still obtain a high specific capacity of 399.8 mA h g<sup>-1</sup> with a capacity retention of nearly 87.7%, indicating that that Cu-VO<sub>x</sub> electrode had excellent reversibility and cycling stability during the charging/discharging process. Fig. 4d shows the rate characteristics of the contrast electrodes at various current densities. Obviously, the rate characteristics of the Cu-VO<sub>x</sub> electrode were much better than those of the contrast electrodes. (The values of the current densities are marked on the graph.) Compared with the contrast materials, the bonding cooperation of V–O bonds in the Cu-VO<sub>x</sub> electrode was stronger, and thus the structure was more stable. The cycling stability of different electrodes at 0.1 A g<sup>-1</sup> was further investigated, as shown in Fig. 4e. The Cu-VO<sub>x</sub> electrode still obtained a high specific capacity of 300 mA h g<sup>-1</sup> after 200 charging/discharging cycles, showing its excellent cycling stability. In addition, the Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes showed poor cycling stability with lower initial specific capacities in the first 30 cycles and a large decrease in specific capacity with increasing the cycling number, which could be attributed to the collapse of the nanoblock structure and the slow activation process. Interestingly, the specific capacity of the K-VO<sub>x</sub> electrode decreased from an initial 423.4 mA h g<sup>-1</sup> to 246.3 mA h g<sup>-1</sup> after 30 cycles at 0.1 A g<sup>-1</sup>, and then the capacity slowly increased in the subsequent cycles, which may be due to the gradual activation process of the material. The Cu-VO<sub>x</sub> electrode demonstrated excellent cycling stability in the charging/discharging cycles, which could be attributed to the increased interlayer distance and high electrical conductivity. Moreover, the lamellar microsphere structure consisting of nanoparticles shortened the ion-transport distance, improved the structural stability, accelerated the electrochemical activation process, and increased the redox kinetics rate.<sup>46–49</sup> The reaction kinetics of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, Fe-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes were analyzed using electrochemical impedance spectroscopy (EIS), respectively, as shown in Fig. 4f. In the equivalent circuit, R<sub>s</sub> represents the Ohmic resistance, R<sub>ct</sub> represents the charge-transfer resistance, Z<sub>w</sub> denotes the Warburg impedance of Zn<sup>2+</sup> diffusion into the bulk phase of the active material, and Q is the constant-phase angle.<sup>37</sup> The Cu-VO<sub>x</sub> electrode exhibited a smaller charge-transfer resistance, as shown in Fig. 4f, indicating that the Cu-VO<sub>x</sub> electrode had an optimal electrical conductivity, which was mainly attributed to the pre-embedding of Cu<sup>2+</sup> to introduce abundant oxygen vacancies in the Cu-VO<sub>x</sub> material. Fig. 4g shows that the Cu-VO<sub>x</sub> electrode had a high initial capacity of 178.8 mA h g<sup>-1</sup> at a high current density of 6 A g<sup>-1</sup>, and kept a specific capacity of 136.7 mA h g<sup>-1</sup> after 2000 cycles with a high capacity retention of 76.5%. This indicated that the Cu-VO<sub>x</sub> electrode had excellent cycling stability at high current density, which could be attributed to



**Fig. 4** (a) First five cyclic voltammetry (CV) curves of the Cu-VO<sub>x</sub> electrode at 0.1 mV s<sup>-1</sup>; (b) GCD curves of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes at a current density of 0.1 A g<sup>-1</sup>, respectively; (c) GCD curves of the Cu-VO<sub>x</sub> electrode at various current densities ranging from 0.1 to 8 A g<sup>-1</sup>; (d) rate capacity of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes at different current densities; (e) cycling performances of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes at 0.1 A g<sup>-1</sup>; (f) Nyquist plots of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes; (g) cycling performance of the Cu-VO<sub>x</sub> electrode at a high current density of 6 A g<sup>-1</sup>.

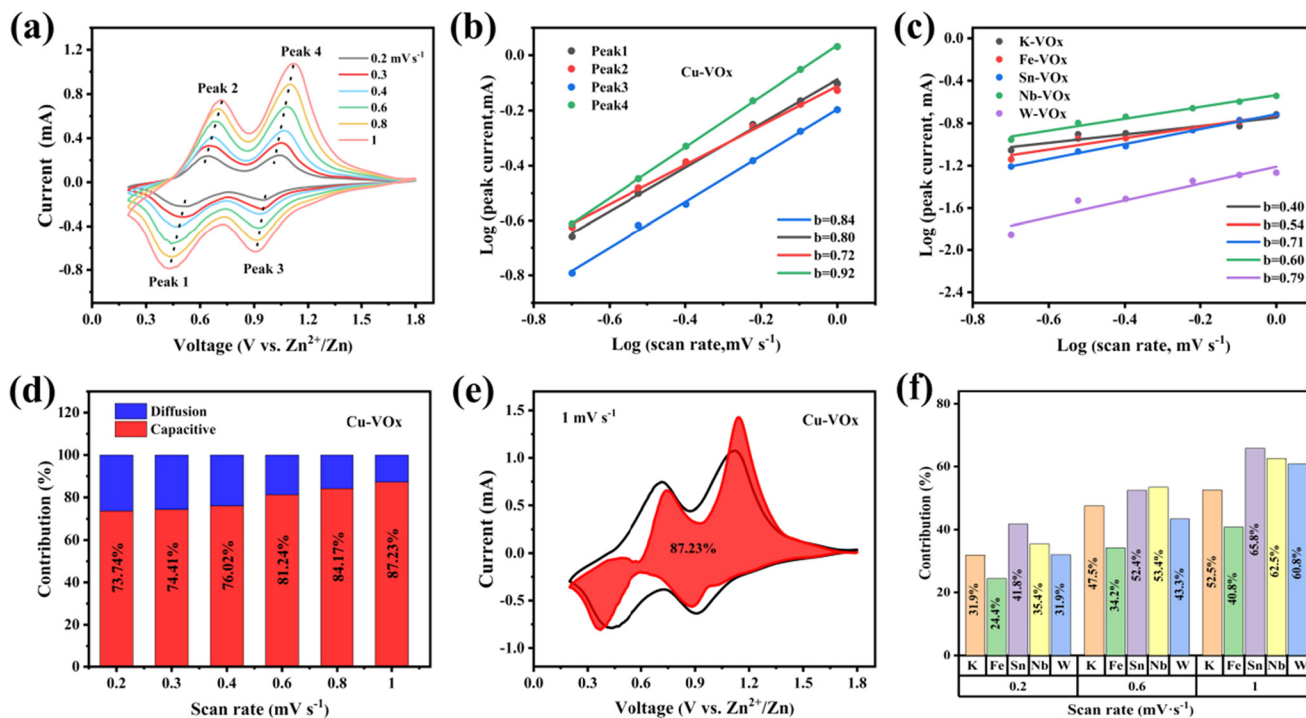
the lamellar microsphere structure of the Cu-VO<sub>x</sub> material consisting of nanoparticles, demonstrating its outperforming structural stability.

To further study the synergistic effect of abundant oxygen vacancies and metal ion pre-embedding to improve the electrochemical performance of the electrodes, the CV curves were investigated to study the electrochemical kinetics and Zn<sup>2+</sup>-storage behavior. Fig. 5a displays the CV curves of the Cu-VO<sub>x</sub> electrode at various scan rates of 0.2, 0.3, 0.4, 0.6, 0.8, and 1 mV s<sup>-1</sup>, respectively. It is clear that with increasing the scan rate, the peak current response became faster. However, the CV curves maintained almost the same shape at different scan rates, indicating that the Cu-VO<sub>x</sub> electrode demonstrated high electrochemical reversibility. The energy-storage mechanism of

the Cu-VO<sub>x</sub> electrode can be analyzed using eqn (1), where  $i$  corresponds to the peak current at different scan rates,  $\nu$  represents the corresponding scan rate, and  $b$  is a variable parameter between 0.5 and 1.

$$i = a\nu^b \quad (1)$$

The energy storage was dominated by a diffusive process (battery behavior) when  $b = 0.5$ , whereas the  $b$  value of 1 indicated the surface-capacitance-controlled process (capacitive behavior).<sup>50</sup> As seen, the energy storage of the Cu-VO<sub>x</sub> electrode was mostly controlled by the surface-capacitance process, as shown in Fig. 5b. Also, the  $b$ -values of peaks 1, 2, 3, 4 for the Cu-VO<sub>x</sub> electrode were 0.84, 0.80, 0.72, and 0.92, respectively. The



**Fig. 5** (a) CV curves of the Cu-VO<sub>x</sub> electrode at various scan rates ranging from 0.2 to 1 mV s<sup>-1</sup>; (b and c)  $\log(i)$  vs.  $\log(v)$  plots of each electrode at specific peak currents of the CV curves; (e) CV curves of the Cu-VO<sub>x</sub> electrode at 1.0 mV s<sup>-1</sup>, showing the capacitive contribution to the total capacity (red region); (d and f) Capacities contributions of the capacitance-controlled and diffusion-limited processes of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, Fe-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes, respectively.

$b$ -values for the K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes are displayed in Fig. 4c for comparison, together with the corresponding analysis of the fitting for peak 1. The  $b$ -values of the K-VO<sub>x</sub> and Fe-VO<sub>x</sub> electrodes were 0.40 and 0.54, respectively. These suggested that surface pseudocapacitance processes dominate energy storage for the K-VO<sub>x</sub> and Fe-VO<sub>x</sub> electrodes, which was also consistent with their relatively low specific capacities as determined by analysis. The diffusion process dominated the energy-storage process for the Cu-VO<sub>x</sub> electrode, which had a comparatively higher specific capacity and superior rate characteristic. The corresponding  $b$ -values of the Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes were 0.71, 0.60, and 0.79, respectively, as shown in Fig. S3† and Fig. 5c. Next, eqn (2), where  $(k_1v)$  denotes the energy obtained by the capacitive reaction and  $(k_2v^{1/2})$  denotes the energy stored by the diffusion process, was used to conduct a more thorough analysis of the ratio of the capacitance-controlled and diffusion-controlled energy-storage processes for the Cu-VO<sub>x</sub> electrode.<sup>51</sup>

$$i = k_1v + k_2v^{1/2} \quad (2)$$

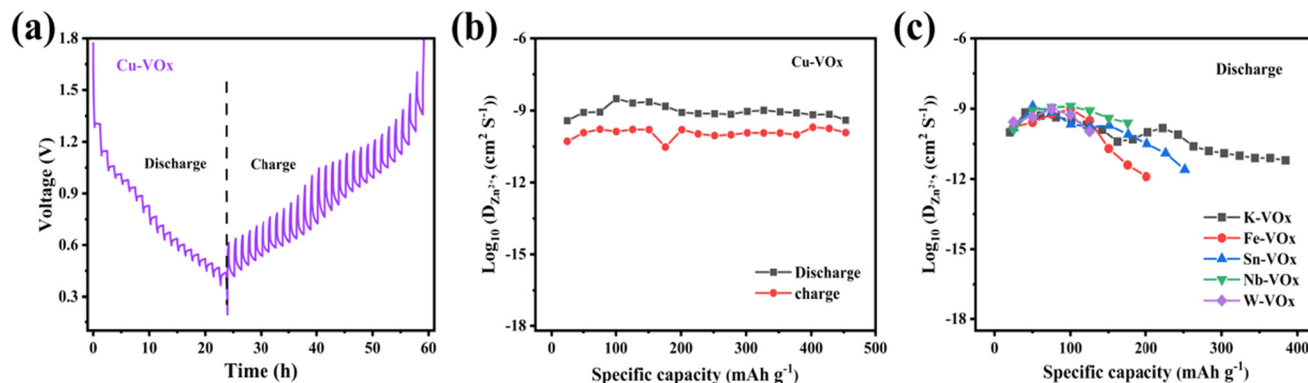
The capacitance contributions of the Cu-VO<sub>x</sub>, K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes at various scan rates are shown in Fig. 5d and f in detail. The surface capacitance contributions of the Cu-VO<sub>x</sub> electrode were 73.74% at 0.2 mV s<sup>-1</sup> and 87.23% at 1.0 mV s<sup>-1</sup>, as shown in Fig. 5d. However, compared to the Cu-VO<sub>x</sub> electrode at the same scanning rate of 1.0 mV s<sup>-1</sup>, the capacitance contributions of the

K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes were only 52.5%, 40.79%, 65.79%, 62.54%, and 60.79%, respectively. Therefore, the Cu-VO<sub>x</sub> electrode exhibited excellent rate performances. The stronger bonding of Cu-O, the stable vanadium-oxygen skeleton, and excellent structural stability were responsible for the high surface capacitance contribution in the Cu-VO<sub>x</sub> electrodes, which also improved their rate properties and cycling stability. Furthermore, the fitted CV plots of the Cu-VO<sub>x</sub> electrode at 1.0 mV s<sup>-1</sup> are displayed in Fig. 5e, where the CV curve with a surface capacitance contribution of 87.23% is displayed in the reddish-brown region.

The galvanostatic intermittent titration method (GITT) was used to further explore the reaction kinetics of the Cu-VO<sub>x</sub> electrode. Fig. 6a displays the GITT curves of the Cu-VO<sub>x</sub> electrode. This was accomplished by repeatedly charging and discharging the zinc-ion battery for 15 min with an 80 mA g<sup>-1</sup> current pulse and then letting it rest for 1 h to allow the cell to relax. Also, the Zn<sup>2+</sup>-diffusion coefficients ( $D_{Zn}^{2+}$ ) for various charging and discharging states were computed using eqn (3):<sup>52</sup>

$$D_{Zn^{2+}} = \frac{4}{\pi\tau} L^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (3)$$

where the value for the diffusion length ( $L$ ) is equivalent to the electrode's thickness,  $\Delta E_s$  represents the voltage change caused by the current pulse, and  $\Delta E_t$  is the voltage evolution for galvanostatic discharging/charging, respectively. The Zn<sup>2+</sup>-diffusion coefficients ( $D_{Zn}^{2+}$ ) of the Cu-VO<sub>x</sub> electrode are



**Fig. 6** (a and b) Discharging–charging GITT curves and corresponding ion-diffusion coefficients for the Cu-VO<sub>x</sub> electrode; (c) corresponding ion-diffusion coefficients for the discharging GITT curves for the K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes, respectively.

depicted in Fig. 6b, which illustrate the charging and discharging process. With the ongoing the discharging and charging process, the diffusion coefficient kept in a stable state. It fluctuated between  $9.42 \times 10^{-9}$  and  $8.51 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  in the discharging state and between  $9.69 \times 10^{-9}$  and  $1.05 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  in the charging state. Additionally, as shown in Fig. 6c, the diffusion coefficients of the K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes all decreased to a greater extent after 10 h, which may be because the material structure collapsed as the number of cycles increased.<sup>53–56</sup> Also, the initial diffusion coefficients of the K-VO<sub>x</sub>, Fe-VO<sub>x</sub>, Sn-VO<sub>x</sub>, Nb-VO<sub>x</sub>, and W-VO<sub>x</sub> electrodes were smaller than that of the Cu-VO<sub>x</sub> electrode in the discharging state. Cu<sup>2+</sup> pre-embedding in VO<sub>x</sub> framework could improve the Zn<sup>2+</sup>-diffusion rate and reaction kinetics, according to the computed results for the Cu-VO<sub>x</sub> electrode, with superior performance compared to the earlier results based on vanadium-based cathodes.

## 4. Conclusions

In this work, a one-step hydrothermal reaction was used to design and successfully prepare different valence metal pre-embedding VO<sub>x</sub> materials. Also, the pre-embedding of different metal ions was performed and had a great influence on the electrochemical performances of the VO<sub>x</sub> compounds. Compared to the contrast electrodes, the Cu-VO<sub>x</sub> electrode achieved excellent electrochemical performance, with a specific capacity of about  $455.9 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and it maintained a high specific capacity of  $357.0 \text{ mA h g}^{-1}$  over 200 charging/discharging cycles. Surprisingly, the Cu-VO<sub>x</sub> electrode demonstrated  $178.8 \text{ mA h g}^{-1}$  at a high current density of  $6 \text{ A g}^{-1}$  and maintained  $128 \text{ mA h g}^{-1}$  over 2000 cycles, showing excellent rate performance. Cu<sup>2+</sup> pre-embedding in VO<sub>x</sub> introduced abundant oxygen vacancies and increased the interlayer distance, which improved the electrical conductivity and structural stability to accelerate the reaction kinetics. In addition, Cu<sup>2+</sup> pre-embedding weakened the binding energy of the V–O bonds, making it easier for Cu-VO<sub>x</sub> to maintain structural stability during charging/discharging cycles. On the

other hand, the construction of thin sheet microspheres composed of nanoparticles increased the structural stability and shortened the distance for ion transport, enabling the Cu-VO<sub>x</sub> electrode to demonstrate high rate characteristics and a long cycling lifespan. This design strategy provides a reference for the design of cathode materials with high electrochemical performances and can accelerate the commercial application of aqueous zinc-ion batteries.

## Author contributions

Juan Xu: methodology, validation, writing original draft. Nengneng Han: conceptualization, investigation, editing. Sihao Chen: conceptualization, investigation. Yahui Zhang: conceptualization, investigation. Yuezhou Jing: conceptualization, investigation. Pibin Bing: conceptualization, editing. Zhongyang Li: conceptualization, review & editing.

## Data availability

Data for this article, including [description of data types] are available at [name of repository] at [URL – format <https://doi.org/10.1039/d4dt01415d>].

## Conflicts of interest

All the authors discussed the results and commented on the manuscript. And, the authors declared that they have no known competing financial interests.

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